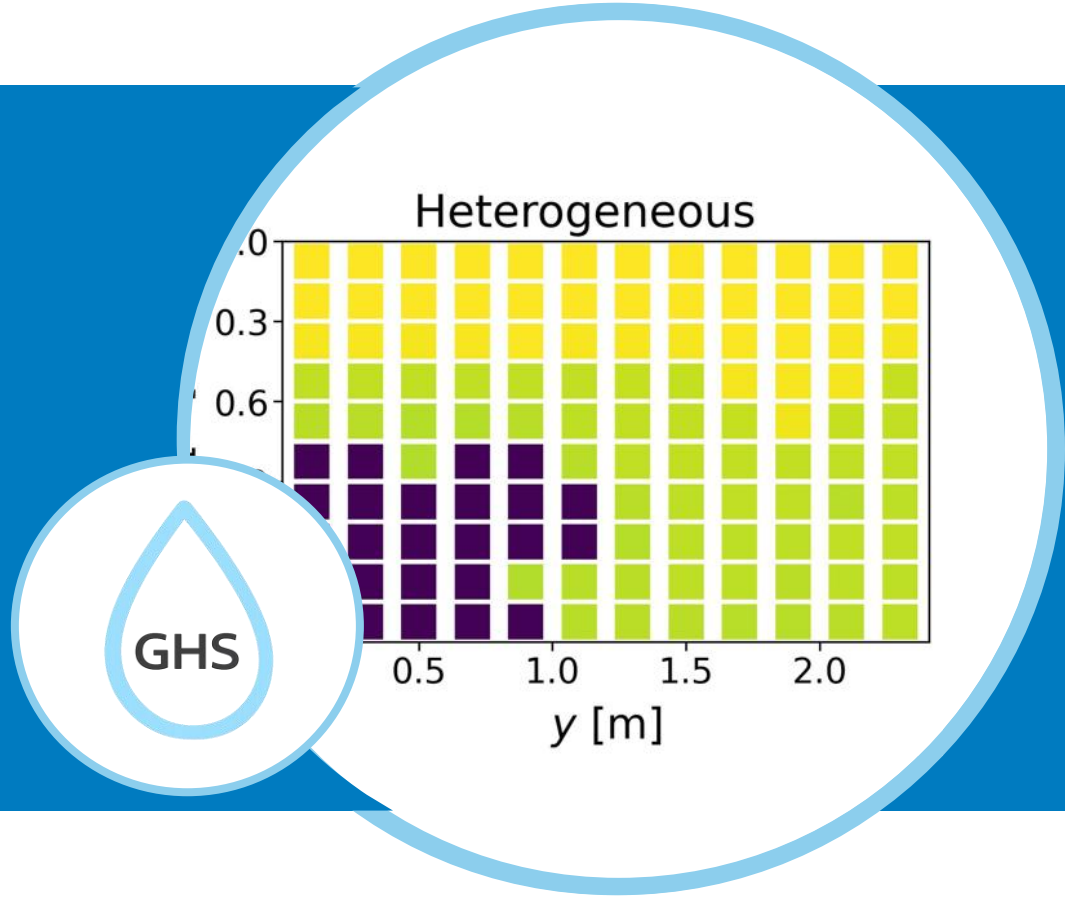
Assessing the Role of Uncertainty on Reactive Transport across Redox-active Porous Media



InterPore

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The Team

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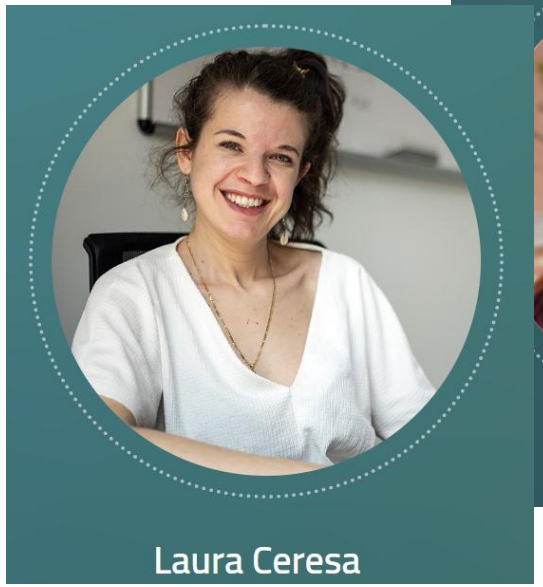
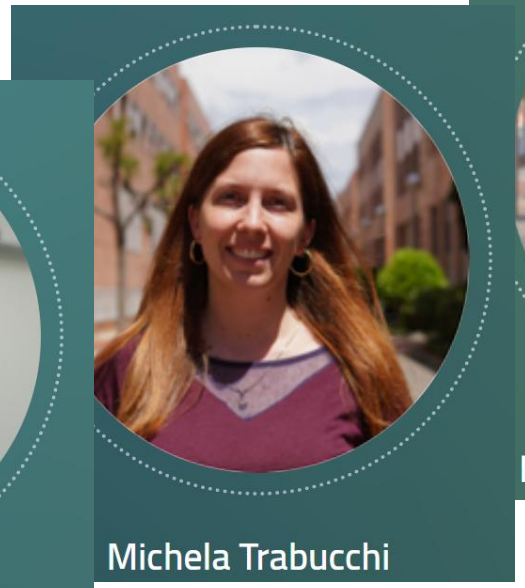


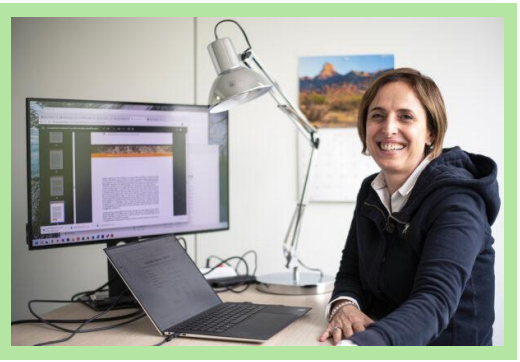
Research Fellow



Research Fellow

Associate Professor

Full Professor



Full Professor

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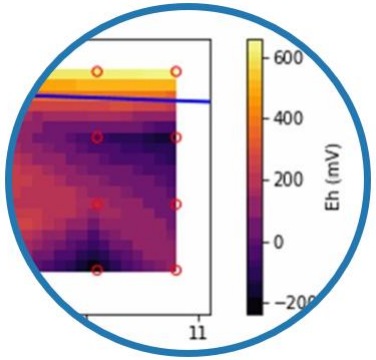
We acknowledge

HETMAR

(PID2023-148543OA-I00)

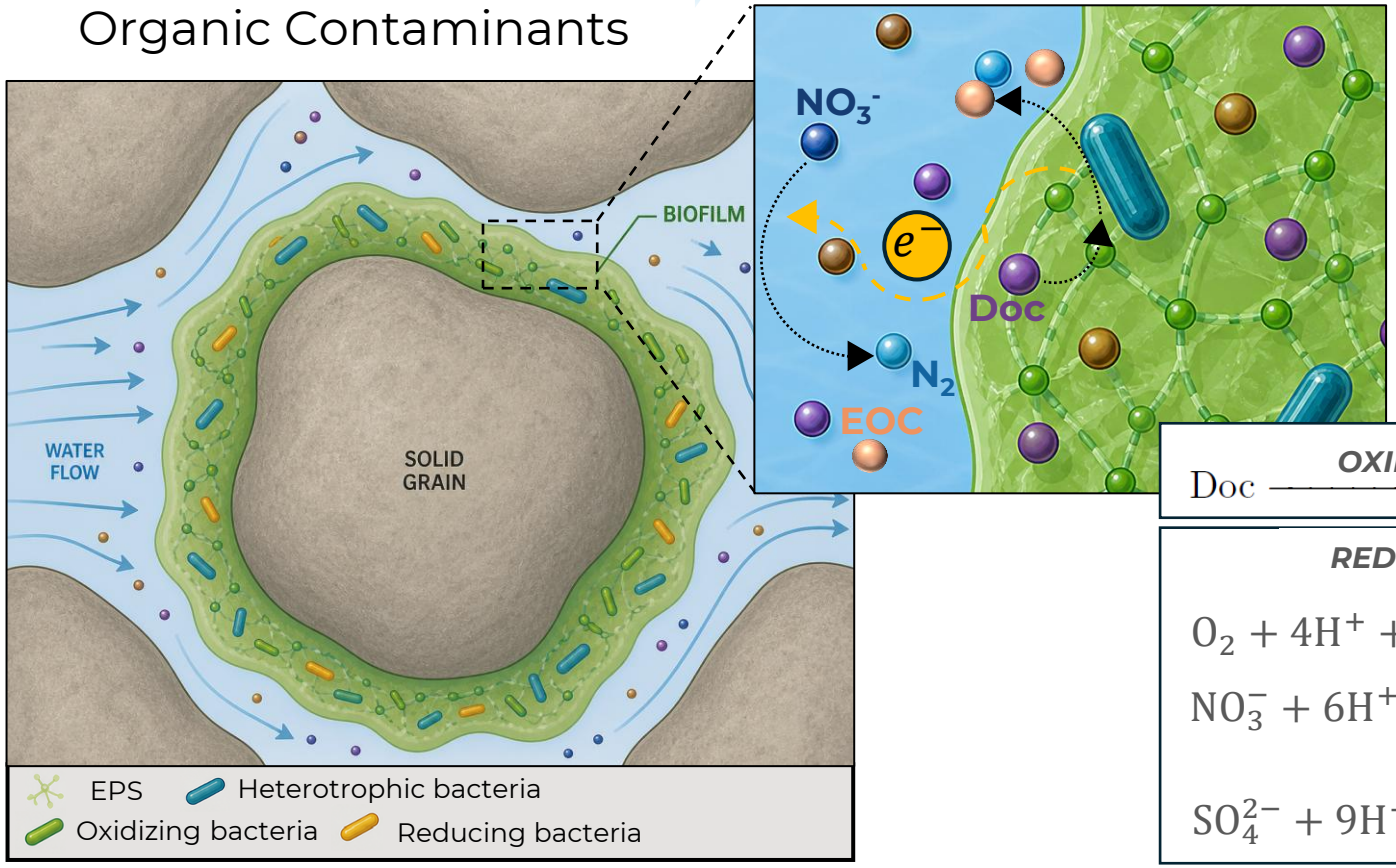
Efecto de la **heterogeneidad geoquímica** en el **destino** de los **compuestos orgánicos emergentes** en actuaciones de **recarga gestionada** de **acuíferos**



Motivation

- Biofilm development
- Fate of Emerging Organic Contaminants

Biogeochemical status of groundwater



$$pe = -\log a_{e^-}$$

$\gg 0$: oxidizing
< 0: reducing

Proxy of redox conditions

$$E_h = \frac{2.3RT}{F} pe$$

Redox potential

$$\mathrm{Doc} \xrightarrow{\text{OXIDATION}} \mathrm{CO_2} + 4e^-$$

REDUCTION processes:

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$$

$$NO_3^- + 6H^+ + 5e^- \leftrightarrow 0.5N_2 + 3H_2O$$

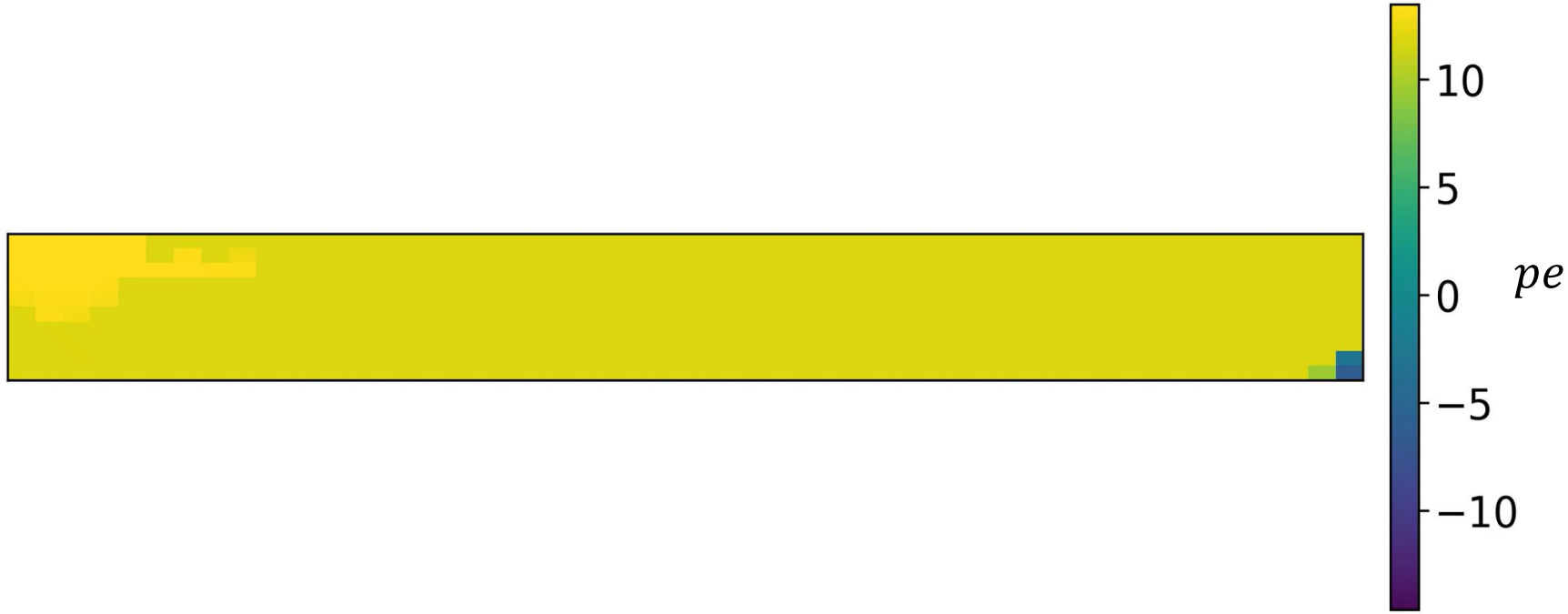
...

$$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O$$

Oxygen
Nitrate
Mn/Fe oxide
Sulfate
$pe \downarrow$

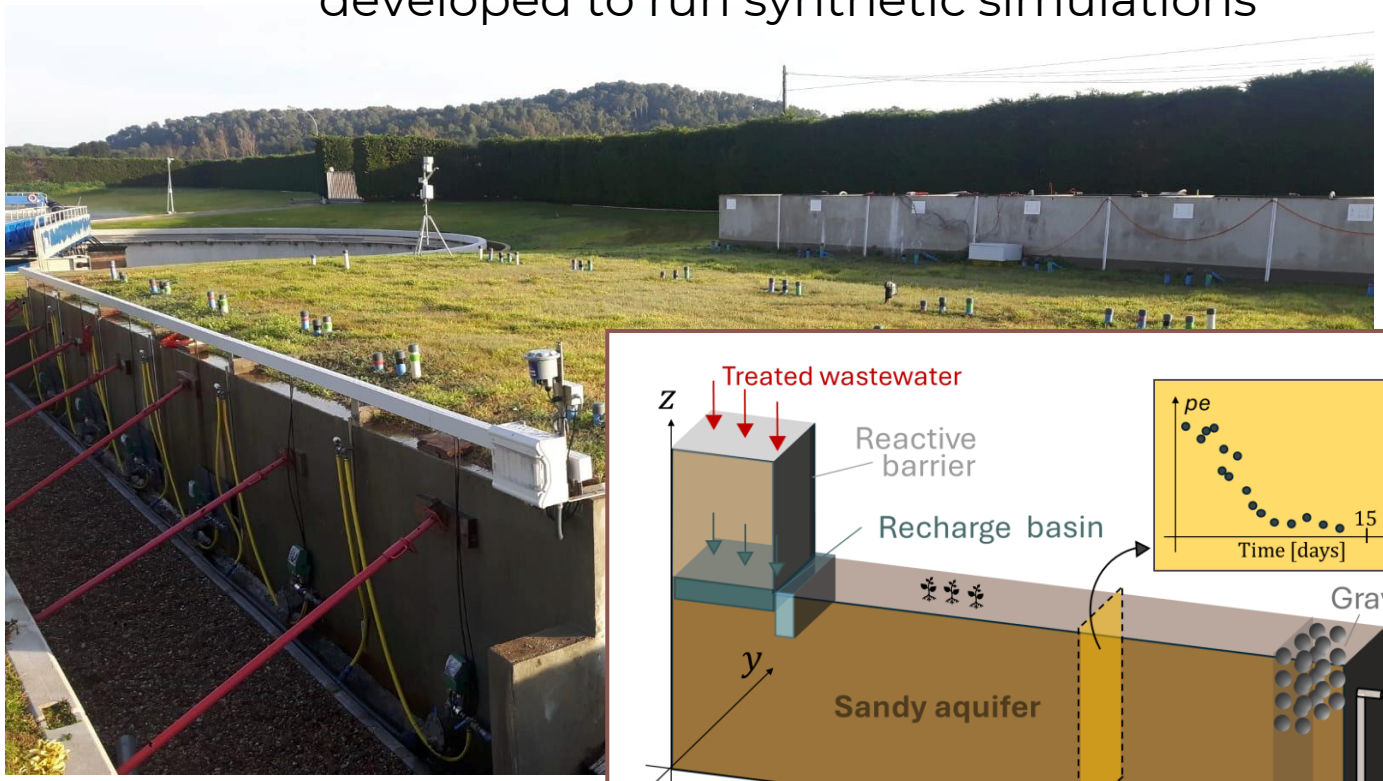
Goal

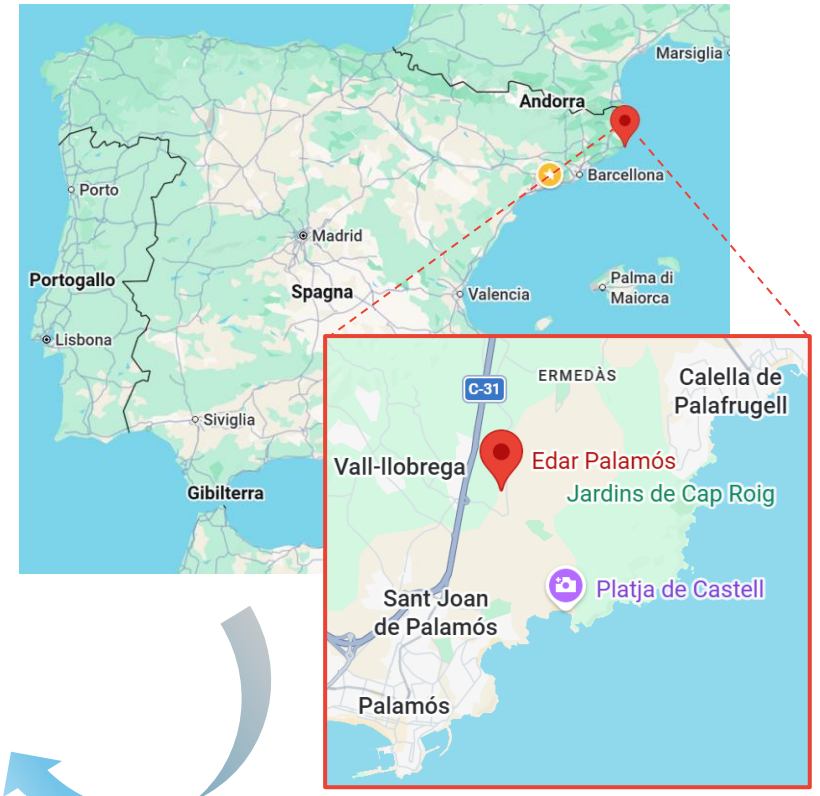
Which is the effect of porous media heterogeneity (e.g., in hydraulic conductivity) on its biogeochemical status?



Conceptual model

The **pilot-scale MAR facility inspiring** the **conceptual model** developed to run synthetic simulations

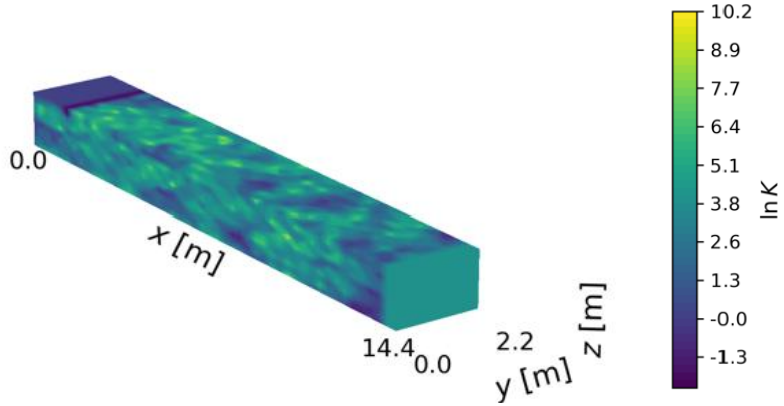




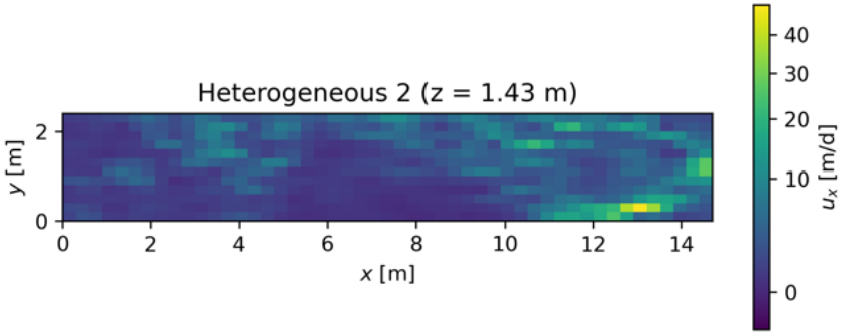
Palamos WWTP, Girona, Spain

Modeling steps

1. Generate ***synthetic heterogeneous hydraulic conductivity realizations*** (SGSIM, GSLIB).



2. Solve the ***subsurface flow equation*** *(MODFLOW 6).*



3. Solve the ***advective dispersive reactive transport equation*** *(MODFLOW 6 + PHREEQCRM).*

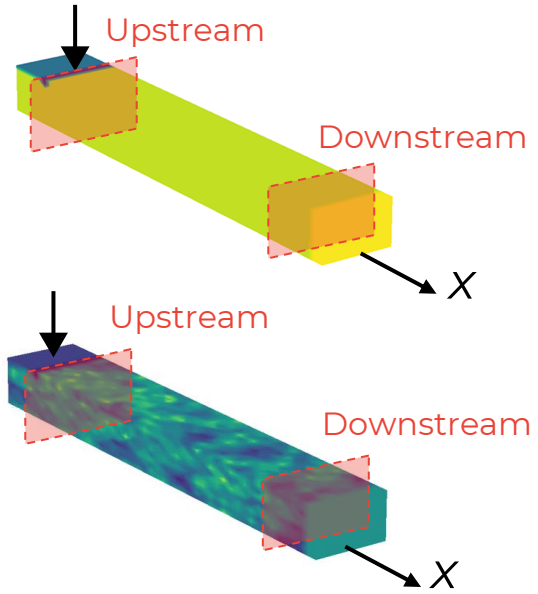
$$\frac{\partial C_i(\boldsymbol{x},t)}{\partial t} = -\boldsymbol{u}(\boldsymbol{x},t)\nabla C_i(\boldsymbol{x},t) + \nabla\left(\boldsymbol{\alpha}|\boldsymbol{u}(\boldsymbol{x},t)|\nabla C_i(\boldsymbol{x},t)\right) \pm \left(\frac{\partial C_i}{\partial t}(\boldsymbol{x},t)\right)_{RXN}$$

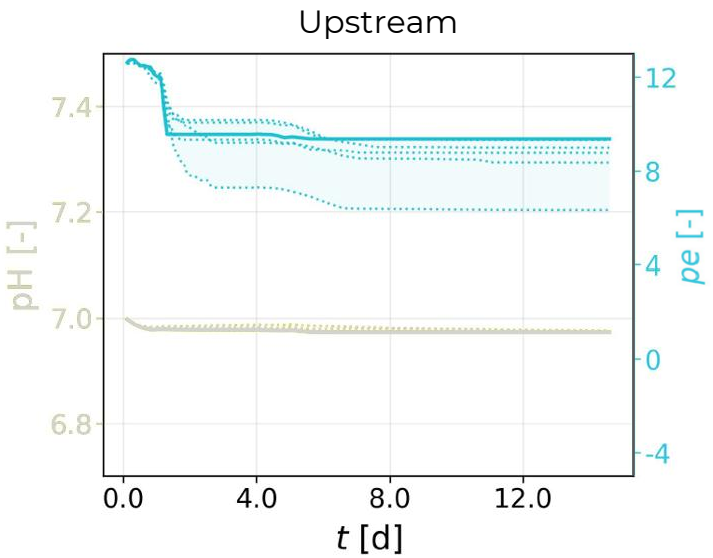
mf6rtm 0.3.1

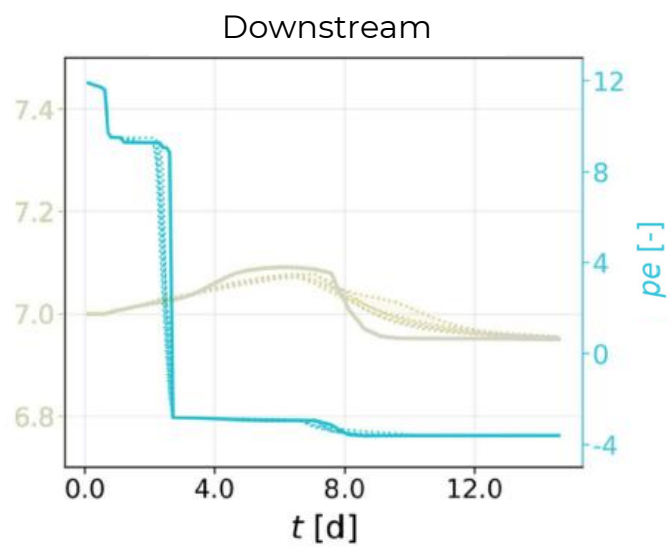
Average vs Local Behavior

Flux-averaged breakthrough curves (BTCs) ➡ $pe(x,t) = \frac{\langle pe(x,y,z,t) q_x(x,y,z,t) \rangle_A}{\langle q_x(x,y,z,t) \rangle_A}$

q_x: Darcy flux along the mean flow direction

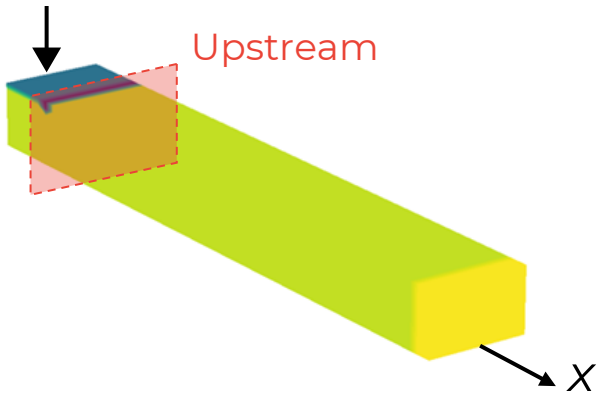




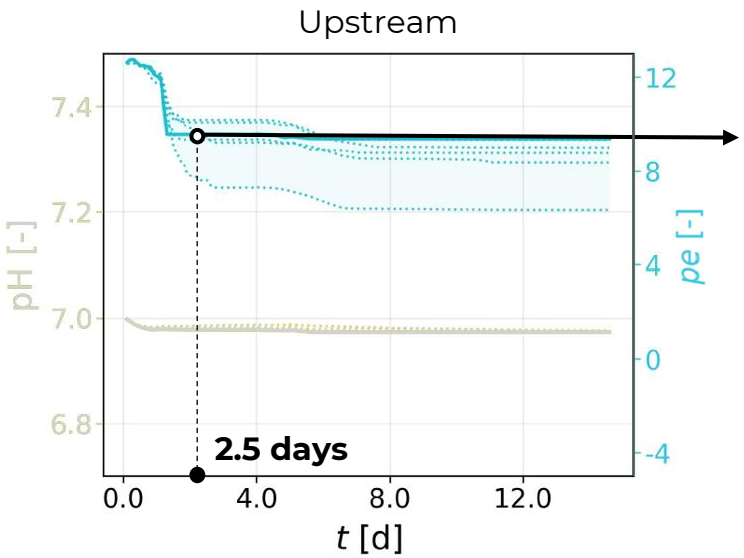


pH — *pe* — Homogeneous ····· Heterogeneous

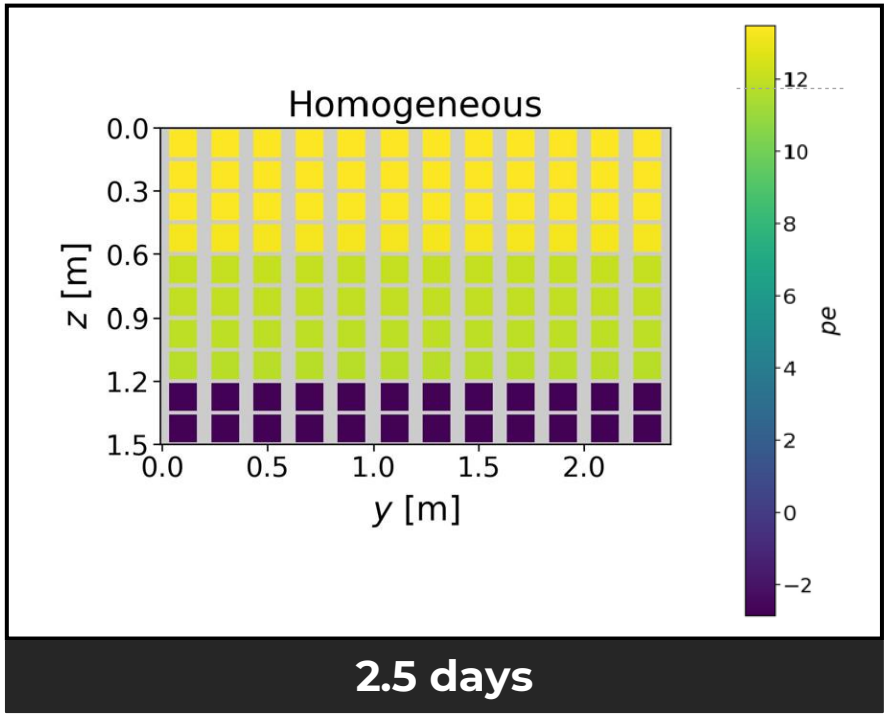
Average vs Local Behavior



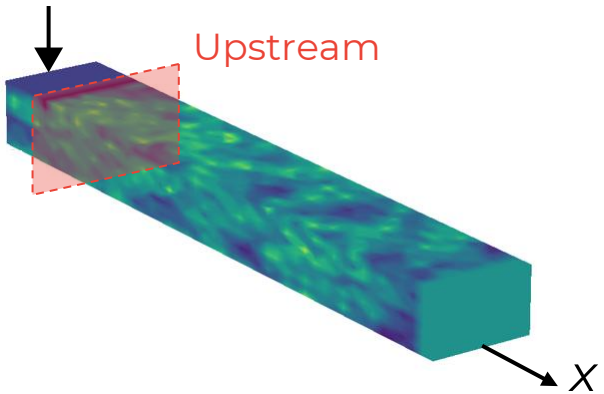
Flux-averaged BTC



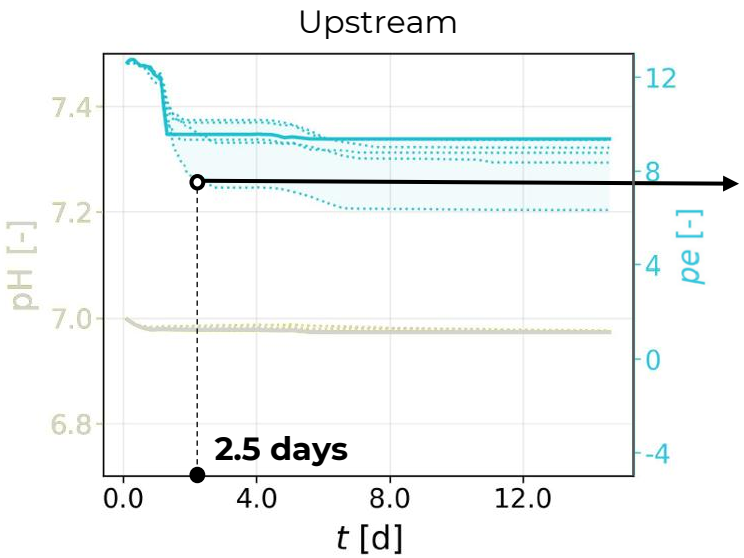
Local behavior



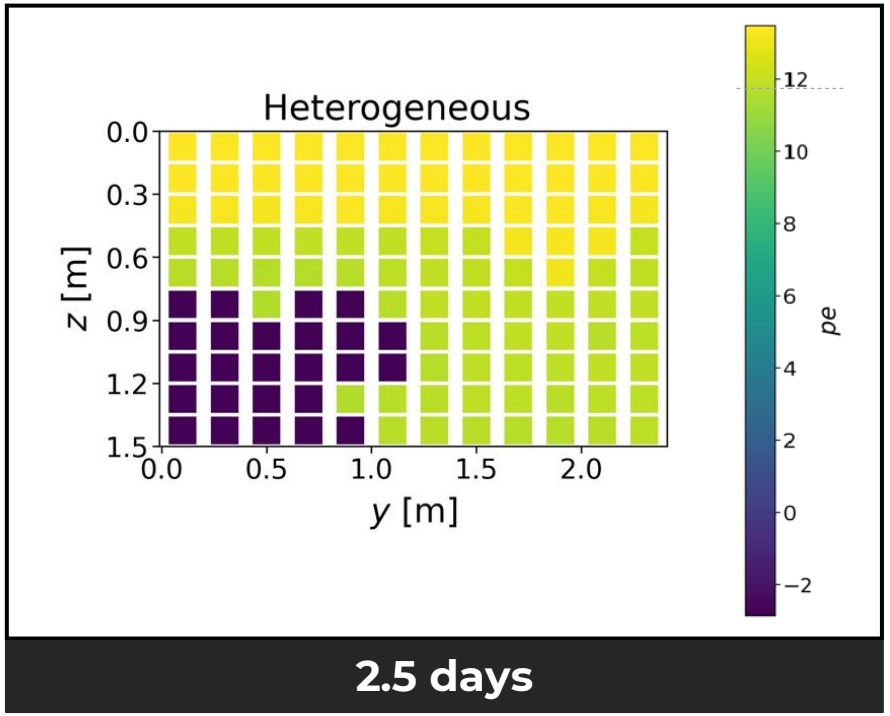
Average vs Local Behavior



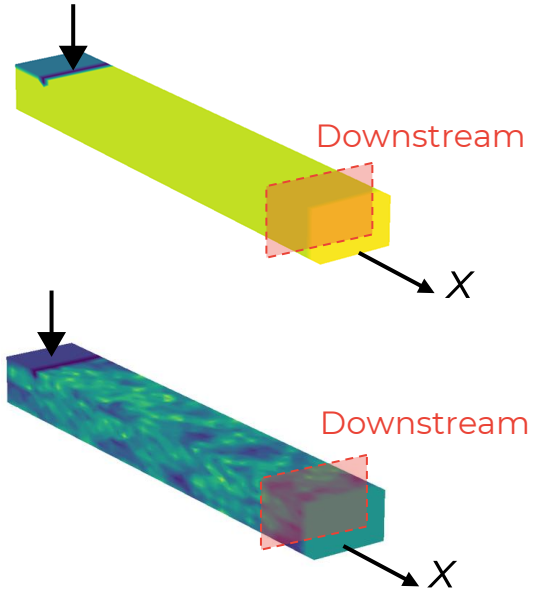
Flux-averaged BTC



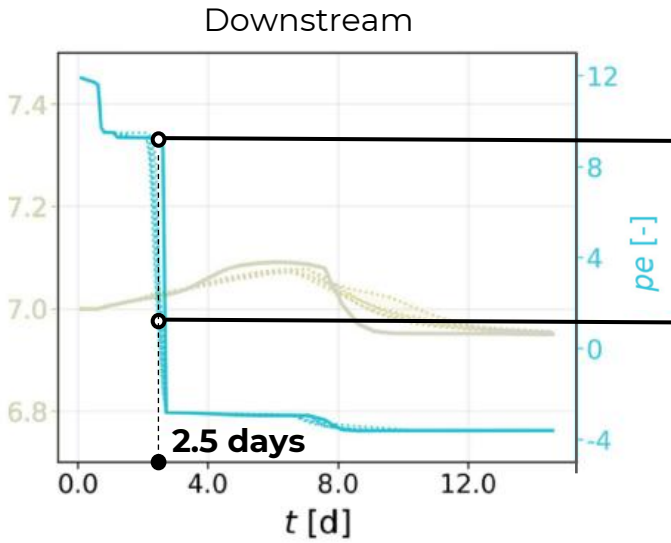
Local behavior



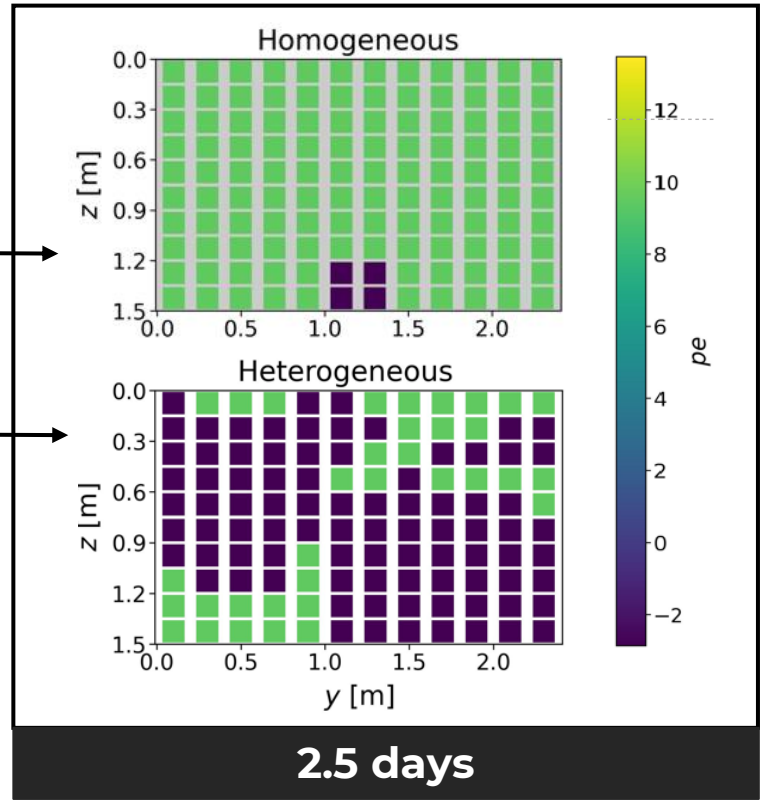
Average vs Local Behavior



Flux-averaged BTC

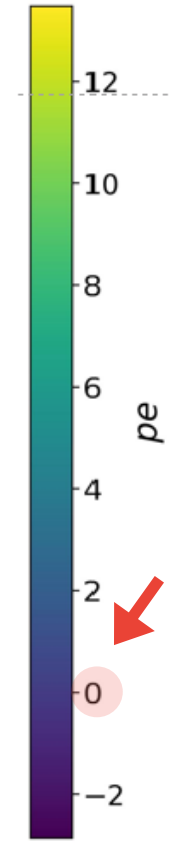


Local behavior



Local Behavior

PV_{50} → *Earliest (dimensionless) time* such that the 50 % cross-section at *x* attains *pe<0*



Local Behavior

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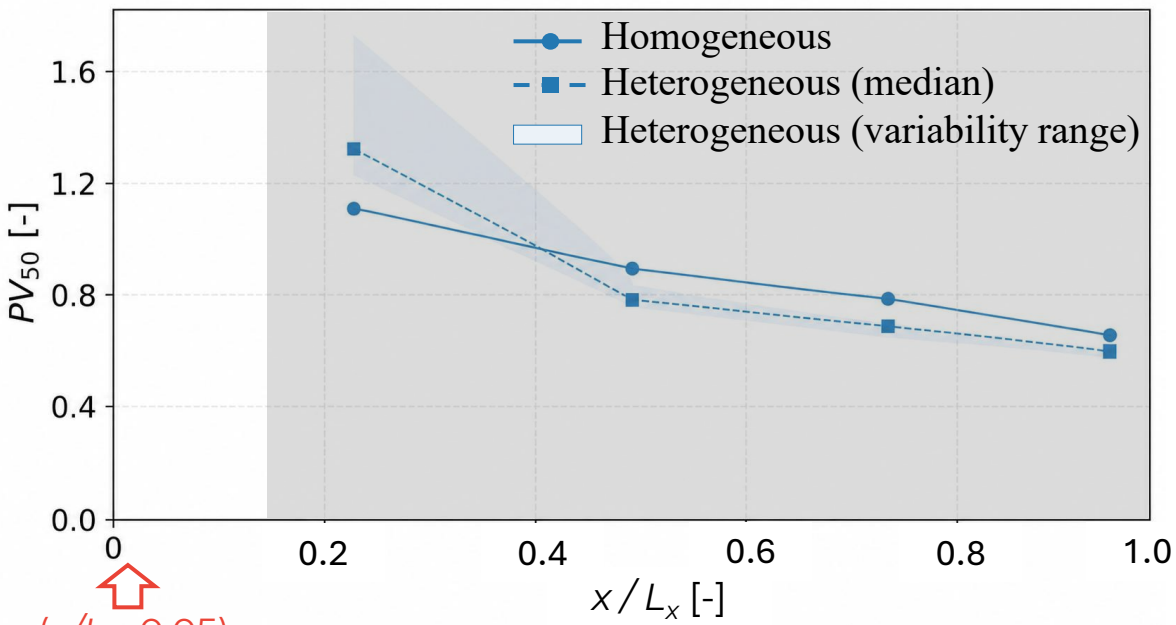
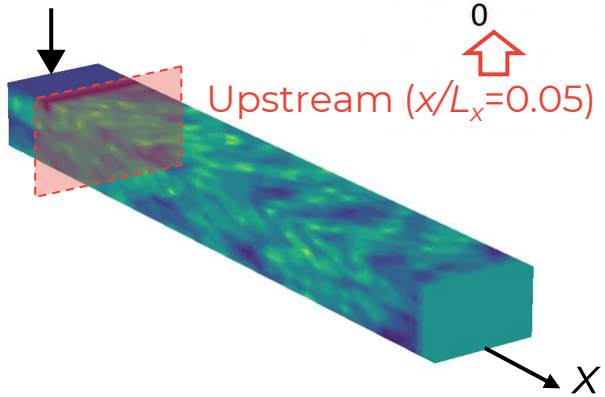
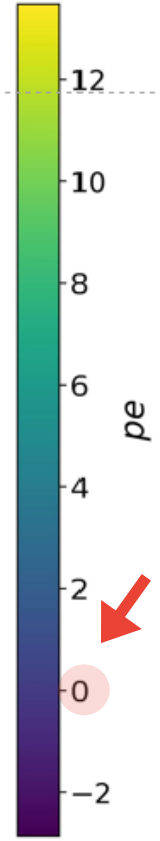
PV_{50} not reached within simulation time (≤111 PVs)







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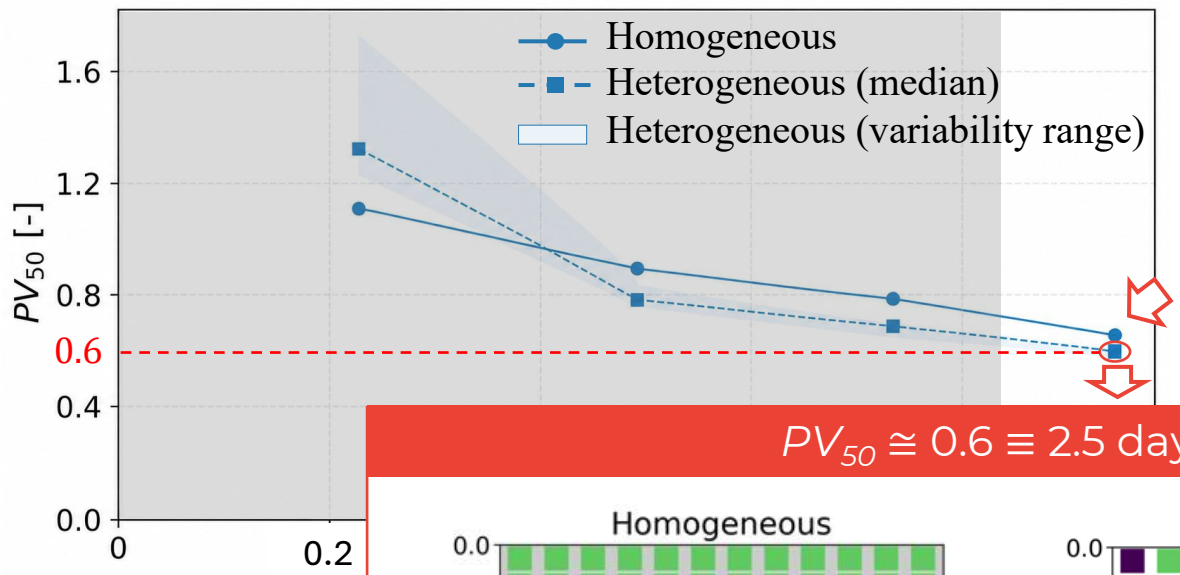
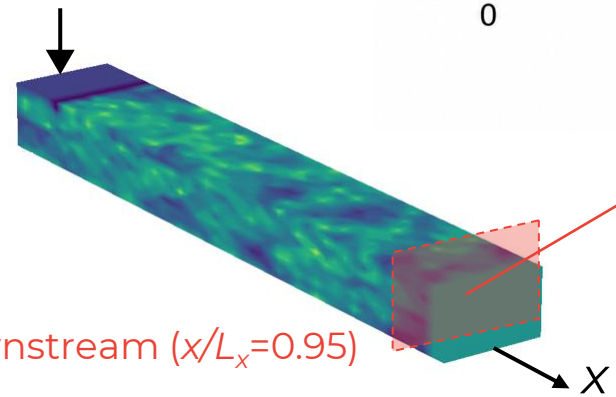
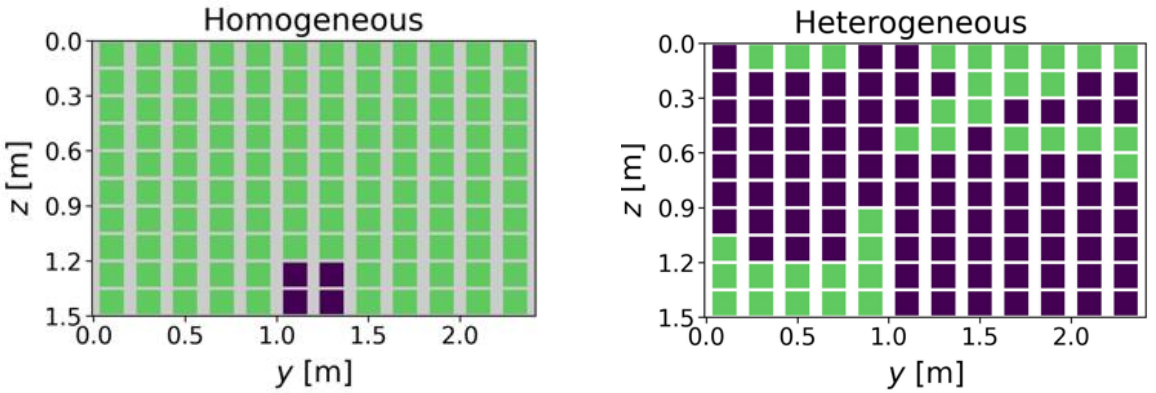
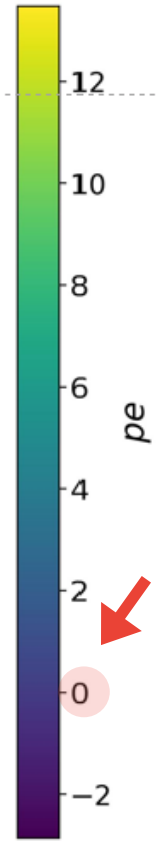


PV_{50} ***reached*** **earlier** in **heterogeneous** porous media



$PV_{50} \cong 0.6 \equiv 2.5$ days





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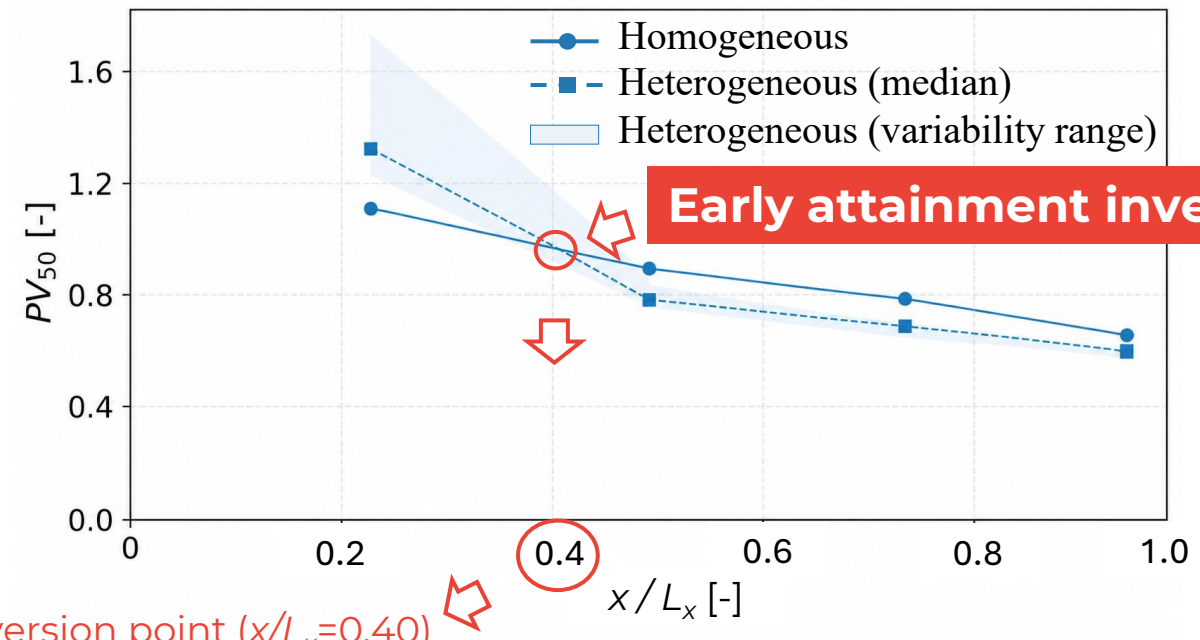

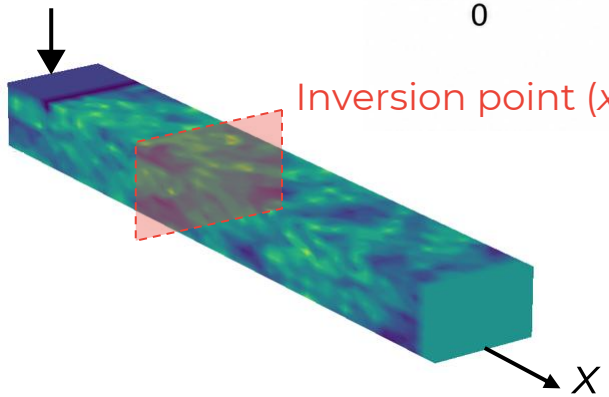

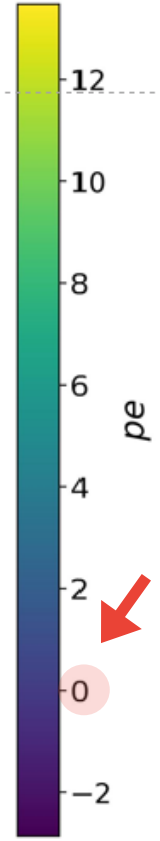

Conclusions

Porous media **HETEROGENEITY**

Promotes local **co-existence of oxidizing & reducing conditions** at the same measurement points.

Accelerates or **delays reaching** a given **local fraction** of **reducing conditions,** depending on **distance** from the **recharge source**.

- Field measurements of redox potential (E_h) should be interpreted with caution: they are representative of spatially integrated signals and tend to over-smooth system's behavior.
  - The impact of hydraulic heterogeneity on pollutant degradation and biofilm development may be systematically underestimated.

Need for **models quantifying uncertainty** in **local redox dynamics** to support MAR design.

Thanks for your attention !

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